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DEVELOPMENT OF ULTRA-THIN FILM
PRESERVATIVE COMPOUNDS

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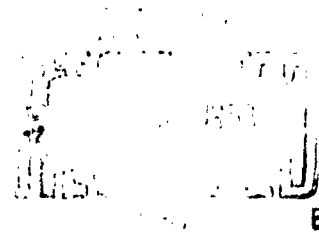
Prepared under Navy, Bureau of Naval Weapons
Contract NOW 63-0293-c

QUARTERLY REPORT NO. 1

Covering Period: 1 Nov. 1962 thru 31 Jan. 1963

FOSTER D. SNELL, INC.

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DEVELOPMENT OF ULTRA-THIN FILM

PRESERVATIVE COMPOUNDS

Prepared under Navy, Bureau of Naval Weapons

Contract NOw 63-0293-c

QUARTERLY REPORT NO. 1

1 November 1962 through 31 January 1963

FOSTER D. SNELL, INC.
29 W. 15th St., N. Y. 11, N. Y.

This report applies
to work on

Contract NOw 61-0855c

ABSTRACT

The controlled cycle condensation humidity cabinet was recalibrated and several materials which had been tested previously were retested. Results corresponded well with previous data. Materials screened during this reporting period included a series of mixed acids and esters of oxidized petroleum fractions, metal and amine soaps, fatty acids and esters, ethoxylated aliphatic amines and amides, petroleum sulfonic acids and their salts and polymeric film formers.

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I. INTRODUCTION

The objective of this contract is the conduct of research and tests to develop the formulation and associated application technics for a material to produce an effective ultra-thin, transparent, corrosion preventive coating for critical metal surfaces. This material is to have the following general properties:

- (a) It shall be capable of providing an effective preservative coating of less than 0.0005 inch thickness.
- (b) It shall produce a firm non-tacky film which permits visual examination of the substrate without removal.
- (c) It shall provide a high degree of corrosion resistance to critical metal surfaces.
- (d) It shall not interfere with the operation nor require removal from complex close tolerance equipment prior to placing such treated equipment in service.
- (e) It shall produce a preservative film which will not interfere with dry film or normal wet-film lubrication.

- (f) It shall not constitute a safety hazard in contact with oxygen nor support combustion after it has been applied to metal surfaces.
- (g) It shall be such as to not require specialized equipment for its application.
- (h) It shall be of such composition as to be non-toxic and shall produce no injurious effects when normal safety precautions are exercised.

Materials which qualify for use in grade 3 materials under Military Specification MIL-C-16173c may satisfy many of the requirements of the present objective. Principal limitations of these materials as presently constituted are: color, tackiness and possibly lack of effectiveness when applied in the required film thickness. If the protection from corrosive attack afforded by these materials is considered adequate under normal conditions of application and use, then the comparable protection afforded by a variety of materials in ultra-thin films (less than 0.0005 inch) tested under identical conditions indicates that sufficient corrosion resistance can be easily obtained. It seems that the principal problem will be the maintenance of this resistance after normal handling. Most of the materials which promise to afford sufficient corrosion resistance are soft, tacky films not likely to maintain the protection level desired after handling.

Most film forming polymers and resins when applied in the desired thickness range by normal application methods tend to leave incomplete or pinholed films. There are organo-functional silicones which are reported to be unusually effective protective coatings in thicknesses of 0.00001 inch. They are reported to have unusually tenacious adhesion to metal substrates and to be completely free of pinholes. These are, at present quite expensive - about \$45.00 per pound on a solids basis - and, even at the coverage obtainable, may prove prohibitively costly to use in the intended areas of application. For best results, the organo-functional silicones require heat cures or aging periods.

II. PREPARATION OF TEST SPECIMENS.

Steel coupons (2" x 4" x 1/8") of SAE 1010 cold-rolled steel were prepared for coating in the following manner:

1. Irregularities, burrs, etc., were ground away from panel edges and corners using 150 grit aluminum oxide wet-or-dry grinding belt running at 1800 rpm. After rinsing in naphtha, faces of the panels were ground in the same manner. Following another rinse, the panel faces were ground with a 350 grit grinding belt. During grinding operations, materials were kept wet with kerosene.
2. After grinding, test faces were finished by polishing with a buffing wheel to a finish of 1 to 3 microns.
3. Excess polishing grit and other foreign matter were removed by washing panels in a 1% solution of Triton X-42 in kerosene. Panels were then degreased in trichloroethylene vapors, rinsed successively in hot naphtha, methanol and allowed to dry. Cleaned panels were wrapped in soft paper and stored in a dessicator until ready for use.
4. Test coupons were dip-coated from respective solutions of candidate materials using a Fischer-Payne dipcoater operating at a withdrawal rate of 1/16 inch per second. Coated panels were dried overnight and then placed in the corrosion test chamber. (For materials requiring special cures or aging, the coating process would be modified accordingly.)

III. CORROSION TEST CHAMBER OPERATION.

The corrosion test chamber used to evaluate materials under this project is described in the Final Report on Development of Ultra-Thin Film Preservative Compounds prepared under Navy, Bureau of Naval Weapons Contract NOw 61-0855c (6 June 1961 through 5 July 1962). This is a modification of the Controlled Cyclic Condensation Humidity Cabinet developed by Minuti and Carroll at Aeronautical Materials Laboratory, NAMC, Philadelphia, Pa.

Test panels were randomly placed in water jacket mountings (taking care to avoid concentrating the location of the same test materials in any one water jacket or mounting column) in order to reduce any bias in testing that might result from position in the test chamber of the test material. For these tests, the test chamber was operated in the following manner.

- | | | |
|--|---|------------------------------|
| 1. Length of test | - | 45, 48 hours |
| 2. Air flow rate into test chamber | - | 1.8 to 2.0 cubic feet/minute |
| 3. Water temperature (air humidifying chamber) | - | 46°C. \pm 5°C. |
| 4. Oil bath temperature (heat exchanger) | - | 70°C. \pm 5°C. |

5. Air temperature (test chamber)	-	50°C. ⁺ 3°C.
6. Dew point (test chamber)	-	39°C. - 41°C.
Relative humidity (test chamber)	-	52%
7. Compressor Timing	-	180 minutes
Cycle On	-	45 minutes
Off	-	135 minutes

Refrigerant return valves on each water jacket were adjusted individually in order to maintain the same rate of cooling. With the test chamber operated as described, a condensation-evaporation cycle on the test panels of 110 minutes wet period and 70 minutes dry period was effected. The periods of this cycle varied from 105 to 120 minutes of condensation and 75 to 60 minutes of dryness.

The operation and control settings for the test chamber were slightly different from those described in previous reports under Contract NOW 61-0855c. These differences are due to a slight modification of the air humidifying chamber and a somewhat greater lag in thermoregulators. However, the resultant cycles and conditions very closely approximated those previously obtained and it is believed that test results should show little variance from prior tests.

IV. EVALUATION OF RESULTS.

Film thicknesses were measured by a wet-film thickness gauge or an Elcometer magnetic film thickness gauge according to the type of film being measured. Tacky or wet films were measured with the wet-film gauge while the Elcometer was used to determine thicknesses of dry, non-tacky films. For these screening tests, film thickness was recorded as greater or lesser than 0.0005 inches. Several materials tested were greater than 0.0005 inches thick, but those were tested so that the testing schedule for other materials could be maintained. Those materials in films thicker than desired which showed significant corrosion protection will be retested later in films of the required thickness while those which did not possess significant corrosion resistant properties in greater than 0.0005 inch thickness will not be further tested.

Materials screened during this reporting period included a series of mixed acids and esters of oxidized petroleum fractions, metal and amine soaps, fatty acids and esters, ethoxylated aliphatic amines and amides, petroleum sulfonic acids and their salts, and polymeric film formers. Repairs to and recalibration of the corrosion test chamber prevented screening of a considerably larger number of materials at this time.

The following materials which were screened during the current period were tested previously under Contract NOW 61-0855c.

Code	Material	Per Cent Surface Rusted	
		Present Test	Previous Test
11	Alox 2028	0.0	0.0
9	Alox 2018	1.0	2.0
24	Nopcohex RD	1.0	1.0
8	Corrosion Inhibitor NPA	0.0	1.0
17	Circosol 2 XH	5.0	3.0

The general agreement between these results indicates that the severity of the conditions of test now and previously are approximately the same. It would have been advisable to include more materials in this comparison which had shown greater surface rusting. Some will be included in further screenings.

A series of materials which have generally good corrosion inhibition properties are mixed acid and esters of oxidized petroleum fractions and their derivatives. Effectiveness of these materials did not seem to be related to either acid number or molecular weight as shown below:

Code	Material	Acid Number	Molecular Weight	Per Cent Rust
31	Alox 100	80	350	0 - 1%
28	Alox 100D	16	422	2%
32	Alox 301	5	---	3%
27	Alox 425*	165	---	4%
30	Alox 600*	50	322	3%
10	Zinc soaps of Alox 600*	---	---	0%
29	Alox 700*	75	700	25%
26	Alox 1963	130	---	3%
9	Alox 2018	170	---	1%
11	Alox 2028	6	---	0%

*Coating thickness greater than 0.0005 inches.

Three fatty esters were screened and two of these, ethylene glycol mono-stearate and sorbitan monoesters of mixed fatty acids gave very good corrosion protection, while the third polyethylene glycol ester of oleic acid was an ineffective rust protectant.

Of three amines screened, only one, a mixture of aliphatic primary, secondary and tertiary amines, Armeen C, proved effective. Two ethoxylated fatty amides Ethomid O/15 and Ethomid HT/60 and two cationic quaternary ammonium salts, Arquad 2HT/75 and Propoquad HT/12 were completely ineffective.

Acid materials screened were generally effective. One which was not too effective under the conditions of this test was a mixture of an oil soluble sulfonic acid of high molecular weight with a hydrophobic alcohol of high boiling point. This material was found to be an effective corrosion inhibitor in five per cent concentration in a MIL-L-6085A Base Oil when tested for 100 hours in the JAN-H-792 humidity cabinet. (See part 3, "Corrosion Prevention Additives" - WADC technical report 53-16 of December 1954.) This apparent discrepancy is probably attributable to the fact that the material in question had previously been tested as a constituent in an oil base and now was tested without a supporting carrier film.

Metal and amine soaps tested were also generally effective. Some of these were, however, applied in thicknesses too great to be considered valid for this application. These will be retested at a later date.

Two film forming materials were tested and were included as potential film carriers of other more effective anti-corrosive materials. Neither of these materials gave very much protection. Protection could be improved, probably, by certain application technics, however, these materials are being considered primarily as carriers for other corrosion resistant materials in later formulations. The deficiency of most of the materials which appear effective, thus far, are their film characteristics.

V. SILICONE OIL FILM.

Dimethyl diethoxy silane which contained 1/4% sulfuric acid catalyst was wiped on to several polished steel panels. The presence of a molecular dimensional silicone oil coating on the metal surface was confirmed by comparing water repellency of treated and untreated steel panels. While these panels did have the water repellency of the silicone films, they did not resist water spot rust as well as untreated panels. This is probably because of the trace amounts of sulfuric acid remaining in the silicone film. Other methods of catalyzing the deposition of a silicone oil film to metal surfaces may be possible which would not leave corrosive products in the deposited film.

VI. SUMMARY AND CONCLUSIONS.

Most materials which were screened in this period were effective metal corrosion protectants under the corrosion test chamber conditions. However, the films of these materials are generally of such quality as to make their protective qualities suspect under normal handling conditions. It will probably be necessary to incorporate successful corrosion inhibitors in film forming carriers.

It is possible that new materials, such as the organo functional silicones (Union Carbide's UCAR, R-101 and R-104) may prove sufficiently effective metal protectors without incorporation of additional inhibitors, but these at present seem prohibitively costly for most ordinary preservative uses.

VII. FUTURE WORK.

Various concentrations of potentially effective corrosion inhibitors will be formulated into film forming carrier solutions and tested by the corrosion test chamber test. In addition, shed storage of successful formulations and testing of these formulations on other metals will be carried out. Lubricity effects will be checked with such instruments as the Falex tester.

Respectfully submitted,

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WM/BB:hn
Oz.
February 27, 1963

VIII. RESULTS OF TESTS

TABLE I

RESULTS OF TESTING IN CORROSION TEST CHAMBER

<u>Code</u>	<u>Material</u>	<u>Thickness</u>	<u>Type Film</u>	<u>Per Cent Surface Rust</u>	<u>Description of Panel</u>
1	Ethylene Glycol Monostearate	<0.5 mils	powdery	1%	Very few light pits.
2	12-Hydroxy Stearic Acid	<0.5 mils	powdery	2%	Very few light pits.
3	Sorbitan Monoesters of Mixed Fatty Acids	<0.5 mils	waxy	None	---
4	Di-Stearyl Dimethyl Ammonium Chloride	<0.5 mils	waxy	100%	Completely pitted surface.
5	Mono Stearyl Tripropyl Ammonium Chloride	<0.5 mils	waxy	100%	Uneven, deep surface rust. 'Speckled'.
6	Polyoxyethylene (5) Oleamide	<0.5 mils	waxy	100%	Very small pits. Completely pitted surface.
7	Polyoxyethylene (50) Hydrogenated Tallow Amide	<0.5 mils	waxy	100%	"Mixed pits" and "Speckled". Uneven, deep surface rust.

TABLE I (Cont'd.)

<u>Code</u>	<u>Material</u>	<u>Thickness</u>	<u>Type Film</u>	<u>Per Cent Surface Rust</u>	<u>Description of Panel</u>
8	Nonyl Phenoxy Acetic Acid	<0.5 mils	tacky	None	---
9	Mixed Acids and Esters of Oxidized Petroleum Fractions	<0.5 mils	waxy	1%	Very few light pits.
*10	Zinc Soaps of Mixed Acids and Esters of Oxidized Petroleum Fractions	>0.5 mils	waxy	None	---
11	Mixed Acids and Esters of Oxidized Petroleum Fractions	<0.5 mils	waxy	None	---
12	Petroleum Sulfonate Base	<0.5 mils	tacky	2%	Very few light pits.
*13	Modified Petroleum Sulfonates Containing Auxiliary Soaps	>0.5 mils	tacky	1%	Very few light pits.
14	Neutral Calcium Petroleum Sulfonate	<0.5 mils	tacky	2%	Very few light pits.
15	Ethylene Diamine Petroleum Sulfonate	<0.5 mils	tacky	1%	Very few light pits.
16	Mixture of High Molecular Weight Sulfonic Acid and Hydrophobic Alcohol	<0.5 mils	tacky	50%	Some deep surface rust. Generally pitted surface.

TABLE I (Cont'd.)

<u>Code</u>	<u>Material</u>	<u>Thickness</u>	<u>Type Film</u>	<u>Per Cent Surface Rust</u>	<u>Description of Panel</u>
17	Naphthenic Acids	< 0.5 mils	tacky	5%	Very light general pitting.
18	Polyoxyethylene (50) Octa Decyl Amine	< 0.5 mils	waxy	100%	Uniform shallow surface rust.
19	1/2 Second Butyrate	< 0.5 mils	non-tacky	100%	Uniform surface rust.
20	Heterocyclic Tertiary Amine	< 0.5 mils	waxy	100%	Uneven, deep surface rust.
<div style="display: flex; align-items: center; justify-content: center;"> <div style="font-size: 4em; margin-right: 10px;">(</div> <div style="text-align: center;"> $\begin{array}{c} \text{CH}_3-(\text{CH}_2)_n - \text{C} \begin{array}{l} \nearrow \text{N-CH}_2 \\ \searrow \text{N-CH}_2 \\ \text{R} \end{array} \end{array}$ </div> <div style="font-size: 4em; margin-left: 10px;">)</div> </div> <p>"R" is derived from oleic acid.</p>					
21	Petroleum Derived Hydrocarbon Resin	< 0.5 mils	non-tacky	10%	Uneven, general light pitting.
22	Polyethylene Glycol Ester of Oleic Acid	< 0.5 mils	waxy	100%	Uneven, deep surface rust.
*23	Mixture of Primary, Secondary and Tertiary Fatty Amines	> 0.5 mils	waxy	None	---
24	Undisclosed	< 0.5 mils	tacky	1%	Very few light pits.
*25	Zinc Linoresinate	> 0.5 mils	tacky	None	---
26	Mixture of Acids and Esters of Oxidized Petroleum Fractions	< 0.5 mils	waxy	3%	Few light pits.

TABLE I (Cont'd.)

<u>Code</u>	<u>Material</u>	<u>Thickness</u>	<u>Type Film</u>	<u>Per Cent Surface Rust</u>	<u>Description of Panel</u>
*27	Mixture of Acids and Esters of Oxidized Petroleum Fractions	> 0.5 mils	waxy	4%	Few light pits.
28	Mixture of Acids and Esters of Oxidized Petroleum Fractions	< 0.5 mils	waxy	2%	Very few light pits.
*29	Mixture of Acids and Esters of Oxidized Petroleum Fractions	> 0.5 mils	waxy	25%	Uneven, shallow surface rust.
*30	Mixture of Acids and Esters of Oxidized Petroleum Fractions	> 0.5 mils	waxy	3%	Few light pits.
*31	Mixture of Acids and Esters of Oxidized Petroleum Fractions	> 0.5 mils	waxy	1%	Very few light pits.
32	Mixture of Acids and Esters of Oxidized Petroleum Fractions	< 0.5 mils	waxy	2%	Very few light pits.

*Thick films.

TABLE II.

MATERIALS EFFECTIVE IN 48 HOUR CORROSION TEST CHAMBER

<u>Effective</u>	
<u>Code</u>	<u>Material</u>
11	Mixed Acids and Esters of Oxidized Petroleum Fractions
3	Sorbitan Esters of Mixed Acids
8	Nonyl Phenoxy Acetic Acid
<u>Moderately Effective</u>	
1	Ethylene Glycol Monostearate
2	12 Hydroxy Stearic Acid
9	Mixed Acids and Esters of Oxidized Petroleum Fractions
26	Mixed Acids and Esters of Oxidized Petroleum Fractions Acid Number - 130
28	Mixed Acids and Esters of Oxidized Petroleum Fractions Acid Number - 16
32	Mixed Acids and Esters of Oxidized Petroleum Fractions Acid Number - 5
14	Neutral Calcium Petroleum Sulfonate
15	Ethylene Diamine Petroleum Sulfonate
12	Petroleum Sulfonate Base
24	Undisclosed (Nopcohex RD)

TABLE III.MANUFACTURER'S DESIGNATIONS OF MATERIALS TESTED.

<u>Code</u>	<u>Manufacturer's Designation</u>	<u>Manufacturer</u>
1	Ethylene glycol monostearate	Glyco Chemicals
2	Hyfac 442-12	Emery Industries
3	Glycomul MA	Glyco Products
4	Arquad 2HT/75	Armour Industrial Chemical Co.
5	Propoquad HT/12	Armour Industrial Chemical Co.
6	Ethomid O/15	Armour Industrial Chemical Co.
7	Ethomid HT/60	Armour Industrial Chemical Co.
8	Corrosion Inhibitor NPA	Geigy Industrial Chemicals
9	Alox 2018	Alox Corporation
10	Zinc soaps of Alox 600	Alox Corporation
11	Alox 2028	Alox Corporation
12	Petrobaze 210	Pennsylvania Refining Corp.
13	Petromix #9	Sonneborn Chemical & Refining Corp.
14	Neutral Calcium Petronate	Sonneborn Chemical & Refining Corp.
15	Ethylene Diamine Petronate	Sonneborn Chemical & Refining Corp.
16	Bondogen	R. T. Vanderbilt Company
17	Circosol 2 XH	Sun Oil Company
18	Ethomeen 18/60	Armour Industrial Chemical Co.
19	EAB 381-20	Eastman Chemical Products, Inc.
20	Amine O	Geigy Industrial Chemicals
21	Piccopale 100	Pennsylvania Industrial Chemical Corp.
22	Nonisol 210	Geigy Industrial Chemicals
23	Armeen C	Armour Industrial Chemical Co.
24	Nopcohex RD	Nopco Chemical Company
25	Zinc Linoresinate	Harshaw Chemical Company
26	Alox 1963	Alox Corporation
27	Alox 425	Alox Corporation
28	Alox 100D	Alox Corporation
29	Alox 700	Alox Corporation
30	Alox 600	Alox Corporation
31	Alox 100	Alox Corporation
32	Alox 301	Alox Corporation